

# Towards fabrication of ordered gallium nanostructures by laser manipulation of neutral atoms: study of self-assembling phenomena

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Surface diffusion has an impact on the lateral resolution of nanostructures in bottom-up atom nanofabrication. In this paper we study the effects of the gallium atoms self-assembled on silicon surfaces (100) patterned with trenches at different slopes. These particular substrate morphologies have been made to enable an effective deposition rate variation along the surface. In this way we experimentally mimic the effect of the atomic flux modulation created by standing wave during an atom nanofabrication experiment. Even if we observe self organization of gallium atoms on the surface, we conclude that the nano-islands are not affected by surface diffusion processes and the effective variation of the deposition rate per unit area is the dominant factor affecting the growth differences along the surface. This result demonstrates that the gallium atoms self-organization should not prevent the observation of a periodic nano-patterning created by atom nano-fabrication techniques.

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## I. INTRODUCTION

In recent years a progress towards the fabrication of nanostructures was made through the laser cooling and manipulation of neutral atomic beams indicated as Atom Nano-Fabrication (ANF) [1]. The ultimate resolution limit in ANF is associated with the quantum-mechanical wave-like nature of atoms. It has been shown that highly collimated beams of laser cooled atoms can be realized with a typical de Broglie wavelength much smaller than the spacing between atoms in a solid. Thus ordered nanostructures can be grown at the single-atom scale. The technique is based on two steps, first the use of laser cooling methods for the high collimation of the atomic beam, second the focusing of atoms through a laser beam in standing wave configuration (light mask). This process produces an ordered pattern with a precise spacing determined by the laser wavelength. Arrays of lines and dots have been already produced using few different atomic species. An important breakthrough for industrial applications will be the demonstration of ANF for technologically relevant materials like Gallium or Indium that are among the key building blocks of modern semiconductor devices.

During ANF the atom-surface interaction and the surface diffusion play a crucial role in determining the lateral resolution of the nanostructures. Indeed surface mobility of the adatoms can increase the structures width or in some cases even wash them out completely, preventing any direct observation of periodic nanostructures created through atom focusing. Furthermore, gallium atoms deposited on substrate are known to self-organize into three dimensional nano-islands randomly distributed on the surface substrate.

In this paper we first describe the realization of our gallium atomic beam and, briefly, the cooling scheme,

that is a crucial step for ANF experiment, then we focus on the analysis of self-organization properties of gallium atoms deposited on a Si substrate surface. Our main interest is to understand how the adatoms self-assembling process could affect the formation of periodic nano-patterned structures created through atom focusing technique. Furthermore, the study of Gallium atoms self-assembled nanostructures is of great interest in material research field. In fact, Gallium self assembled nano-islands are known to be good precursors for bulk synthesis of Silicon nanowires [2].

## II. EXPERIMENTAL

*a. Vacuum system.* The experimental scheme for the vacuum system (Fig. 1) has been carefully planned according to the following criteria: a) keep the system as simple and standard as possible within the current UHV technologies; b) have the possibility to extend and implement the set-up into a Molecular Beam Epitaxy (MBE) system; c) allow the optical access needed for the laser cooling and manipulation of Gallium atoms.

The vacuum chamber can be divided in three regions: I) production of the Gallium atomic beam; II) atom collimation through both mechanical (skimmer) and optical (laser cooling) means; III) optical focusing and deposition of the atoms on a substrate. The chamber is equipped with several viewports AR(Anti-Reflection) coated for the relevant optical wavelength to allow optical collimation, focusing and probing of the atomic beam.

The atomic source is a VTS-Cretec Gallium effusion cell (Dual Filament) with a 1 mm insert in its PBN (Pyrolytic-Bore-Nitrate) crucible. The dual filament configuration prevents the Gallium to condense, leading to possible damaging of the oven. The effusion cell is operated at

a temperature of about 1000 °C and provides an atomic flux of about  $5 \cdot 10^{14}$  atoms/s calculated from the Knudsen law. For the deposition of Gallium nanostructures we need a well collimated high flux atomic beam. To have a first collimation we geometrically cut the flux using two skimmers with 1 mm size and 0.8 mm size respectively, placed at a short distance after the Gallium source. A better collimation stage imposes the use of laser cooling techniques on the transverse atomic distribution. The longitudinal mean velocity, being of the order of  $v_L = 690$  m/s, is not affected by transverse laser collimation.

The last part of the vacuum system is devoted to the optical focusing onto a substrate. The cooling and focusing regions are kept under UHV (better than  $10^{-7}$  Pa) conditions by two ion pumps.

The arrangement described above was set up together with a complementary optical part (laser sources and optics) to demonstrate laser cooling and manipulation of gallium atoms for nanofabrication of ordered structures [3].

*b. Atomic Physics.* The Gallium element ( $Z=31$ ) has two main isotopes  $^{69}\text{Ga}$  (60.1%) and  $^{71}\text{Ga}$  (39.9%), both with nuclear spin  $I=3/2$  and its electronic configuration leads to a ground state  $4p^2P_{1/2}$ . The Gallium atom is a complex atom from the atomic physicist's point of view and there is no closed transition from the true ground state suitable for laser cooling. Our choice about the cooling scheme has been to use the new blue/violet NICHIA laser diodes at 403 nm and 417 nm to investigate two-colour laser cooling on the P-S transitions (Fig. 2). Another scheme of laser cooling at 294 nm (by frequency doubling a Dye laser), based on a closed transition between the  $P_{3/2}$  and  $D_{5/2}$  states, is in use at Colorado State University by the group of Siu Au Lee [4].

*c. Gallium self-assembled nanostructures.* Depositions of gallium neutral atoms were made on Silicon surfaces (100), kept at room temperature, without applying the cooling beams and the standing wave for atom focusing on substrates in order to test solely their self-assembling properties.

The patterned substrates are obtained using standard process techniques and process integration schemes currently used in microelectronics [5]. All substrates used for our experiments have been chemically etched by a solution of HF and deionized H<sub>2</sub>O (1:50 at room temperature for 20 s) in order to remove the native oxidation of the silicon surface.

We performed Transmission Electron Microscopy (TEM) analysis of the deposited samples using a JEOL JEM-2010 field emission transmission electron microscope operating at 200 KV. The instrument is also equipped with a GATAN imaging filter and with an Oxford Instruments LZ5 windowless energy dispersive X-ray spectrometer (EDS).

### III. RESULTS AND DISCUSSION

We investigated experimentally the role of the different photon-atom interactions provided by the violet 403 nm and blue 417 nm lasers [3] and, within this exploratory work, we obtained evidence for laser conditioning of gallium atoms, when at least one laser acted on the blue side of one of the transitions shown in fig. 2. These results open up the way for the systematic study of gallium laser cooling and ANF.

It is beyond the aim of this paper a full description of the atomic physics results, therefore we focus on the self-assembled nanostructures obtained in our deposition experiment from the unconditioned atom beam.

We needed to understand if the Gallium atoms self-assembling properties could prevent any direct observation of nano-patterning during an ANF experiment, without applying in the experiment, at the moment, a standing wave for the atom focusing. For this reason we have chosen some particular substrate morphologies made to enable an effective variation of the deposition rate on the the surface substrate by using silicon substrates with different trenches. In fact, we varied the substrate surface exposed to the atomic Gallium incoming flux by modulating the slope of this surface with respect to the flux direction, as emphasized in the schemes drawn in fig. 3 (a and b). In such a way we simulated a variation of the atomic deposition rate in a similar fashion to that expected during an ANF experiment.

In fig. 3 TEM images of Gallium nanostructures self-assembled on two silicon substrates differently patterned by the trenches are shown. The aim of the comparison was to characterize the Gallium deposition on different slopes of the substrate surface, and therefore to characterize different conditions of deposited thickness. The depositions were made with an exposition time of 90 minutes keeping the substrates at room temperature. For both surfaces of Figs. 3(a) and 3(b) we found that the gallium nanostructures thickness varies along the substrate surface as a function of where is the angle of the slope. In spite of spontaneous organization of 3D islands, this result gives evidence that in our deposition process the Gallium nanostructures grow in a limited diffusion regime. Thus the effective modulation of the deposition rate along the surface is the dominant factor affecting the growth. Indeed, in the case of self-assembled nanostructures an increase of the diffusion barrier for the adatoms from the centre of an island to its edge occurs [6]. This diffusion barrier may be considered the analogous of the Ehrlich-Schwoebel barrier in homoepitaxy. Therefore we believe that the self assembly properties of Gallium should not prevent the direct observation of a periodic modulation at least of the average dimensions of Gallium nanostructures created through atom focusing, when a sufficient percentage of the gallium atoms forming the atomic beam are manipulated by a standing wave.

By TEM analysis it was also possible to characterize the cluster size distribution at different growth regime

(Fig. 4). The Gallium clusters turn out to grow in the Volmer-Weber mode [7, 8]. The nanoparticles are formed after self-organization of vapour condensing on partially wetting (or partially drying) substrates. The Gallium melting point is 29.8 °C, but in the case of sub-micrometric nanostructures this value decreases hence our deposited gallium consisted of liquid droplets [9].

The growth condition is represented by the relation:

$$\Gamma_{sv} - \Gamma_{lv} < \Gamma_{sl} < \Gamma_{sv} + \Gamma_{lv} \quad (1)$$

where  $\Gamma_{sl}, \Gamma_{sv}, \Gamma_{lv}$  are the free energies per unit area of the substrate solid - deposit liquid, substrate solid-vapour and deposit liquid-vapour interfaces, respectively. In these cases the growth process follows different regimes: the nucleation and growth of individual and immobile droplets, the static coalescence of droplets when the surface coverage saturates and the new nucleation of small particles in the area cleaned by previous coalescence phenomena [7]. In fact, by increasing the deposition time we find a bimodal nano-droplets size distribution: a bell-shaped part, due to coalescence, and a tail, caused by renucleation and growth of small particles during deposition, as shown in fig. 4 (d)-(f) at different deposition times. By several TEM analysis with energy filtered imaging technique, as in fig. 5, we also observed that the gallium nano-islands were surrounded by native Ga oxide with an average thickness of about 5 nm. This oxide thickness is determined by sample exposure to ambient air. The smallest particles formed were completely oxidized.

## IV. CONCLUSIONS

In this paper we have studied the behaviour of self-assembled Gallium nano-islands on Silicon surfaces (100) in order to assess possible limitations on the control of nano-structured pattern created during our future ANF experiment. From the experimental results we observed that the Gallium self- assembled nanostructures grow in a limited diffusion regime of the Gallium atoms on the surface. For this reason the average dimensions of the nano-islands followed the flux modulation along the surface. This experimental evidence points out that the self-assembling process of the gallium adatoms on the substrate surface will not prevent the direct observation of a periodic nano-patterning created by ANF technique, if a sufficient percentage of Gallium atoms is manipulated by the standing wave. We are now pursuing our investigation to clarify the minimum percentage of laser manipulated Gallium atoms in the beam ensuring efficient nanopatterned depositions.

## V. ACKNOWLEDGEMENTS

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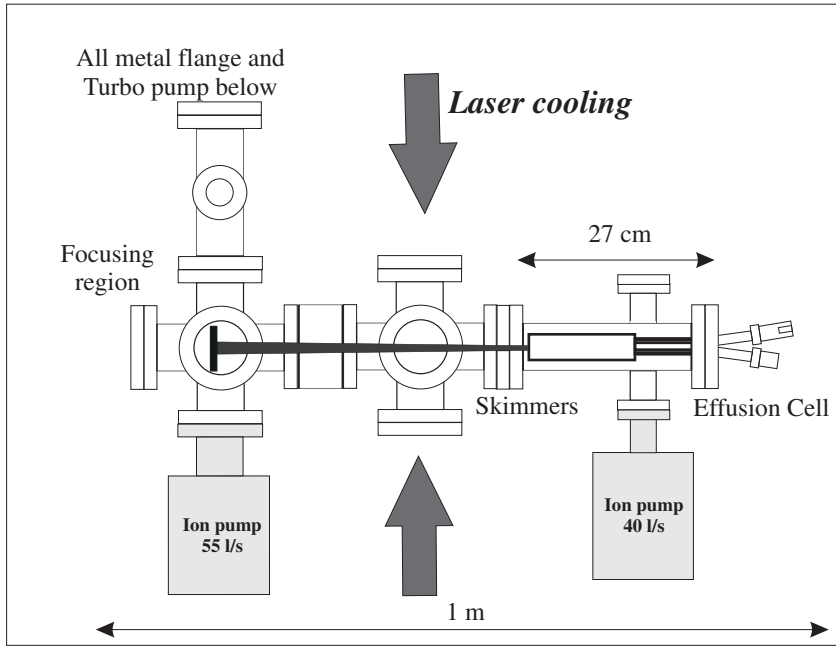


FIG. 1: Vacuum system for the production of a Gallium atomic beam.

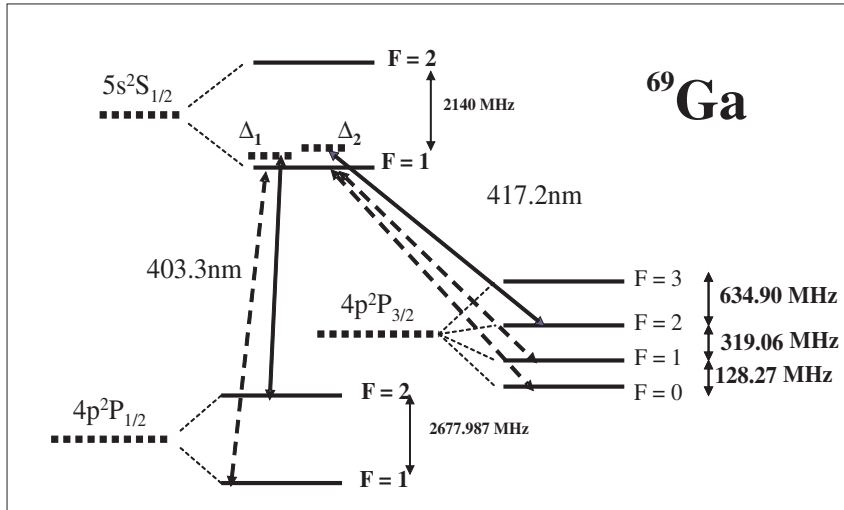


FIG. 2: Hyperfine splittings for the  $^{69}\text{Ga}$  isotope and a choice of fluorescence cycles for laser cooling and repumping. To close the cooling transitions from the ground states (P states) we need blue radiation at 403 nm and 417 nm.

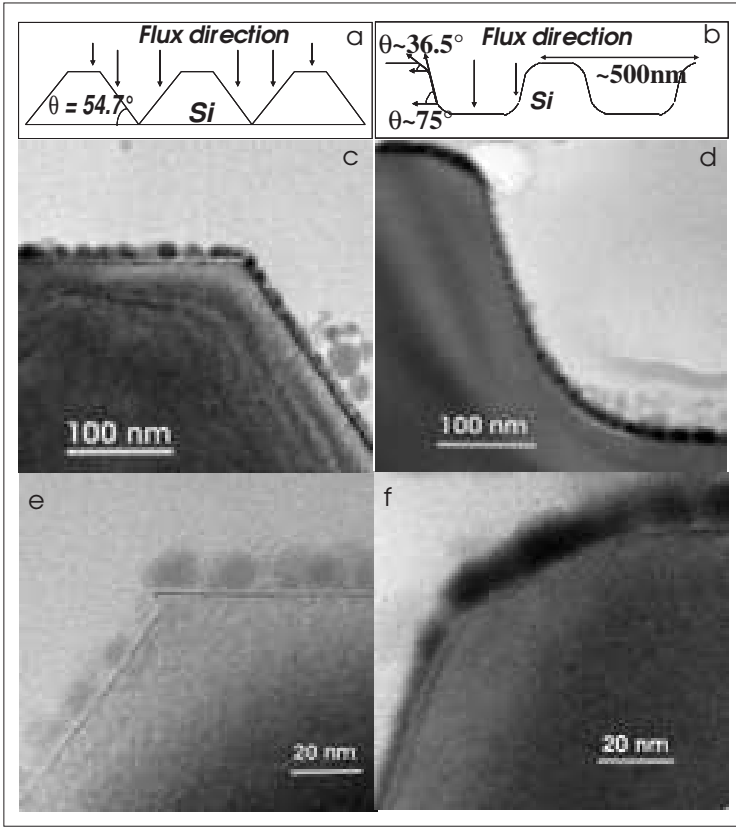


FIG. 3: In (a) and (b) schemes of the trenches with different slopes realized on the silicon substrates are shown. In (c)-(f) are given TEM images in plan view at different magnifications of gallium nano-islands self assembled on Si (100) surfaces patterned with trenches. The images c), e) and d), f) correspond to the two schemes for the trenches at different slopes, respectively a) and b). In both cases it is evident how the gallium nano-islands thickness changes linearly with the slopes following a law.

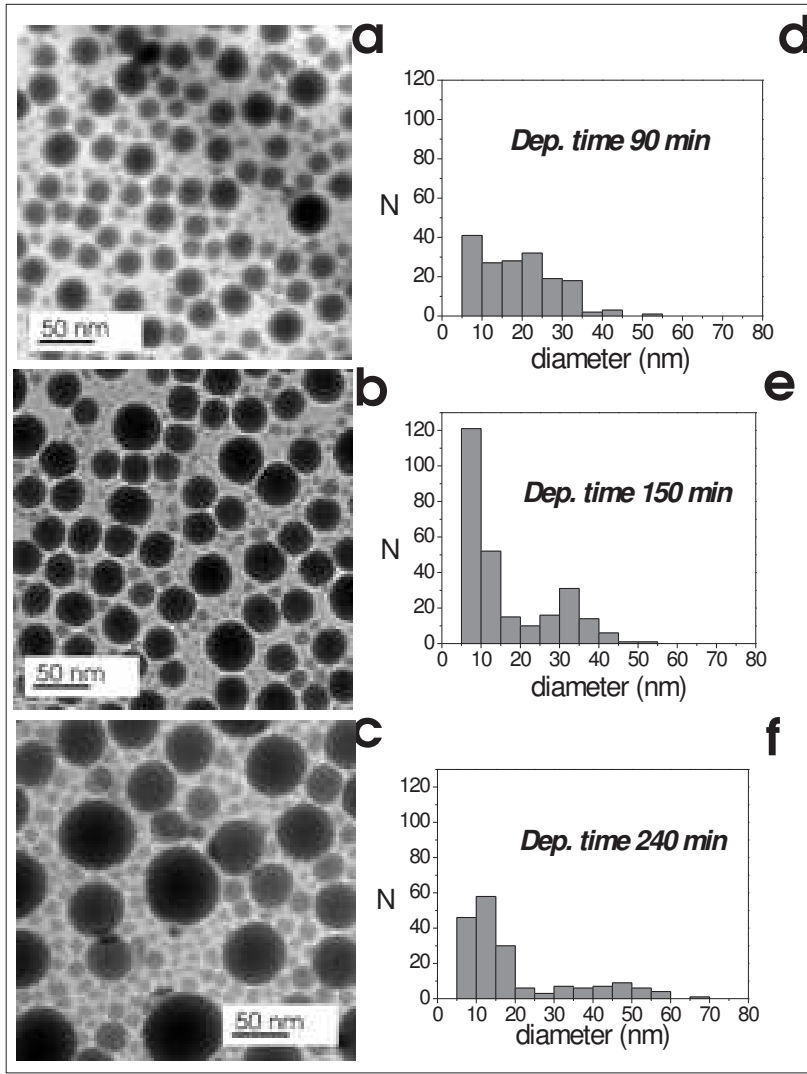


FIG. 4: In (a), (b) and (c) are shown TEM images in plan view of gallium nano-islands self-assembled on Si (100) flat surfaces at different deposition times, 90, 150 and 240 minutes respectively. In (d), (e) and (f) histograms of the number of nanoparticles  $N$  versus the diameter  $d$  in nm.

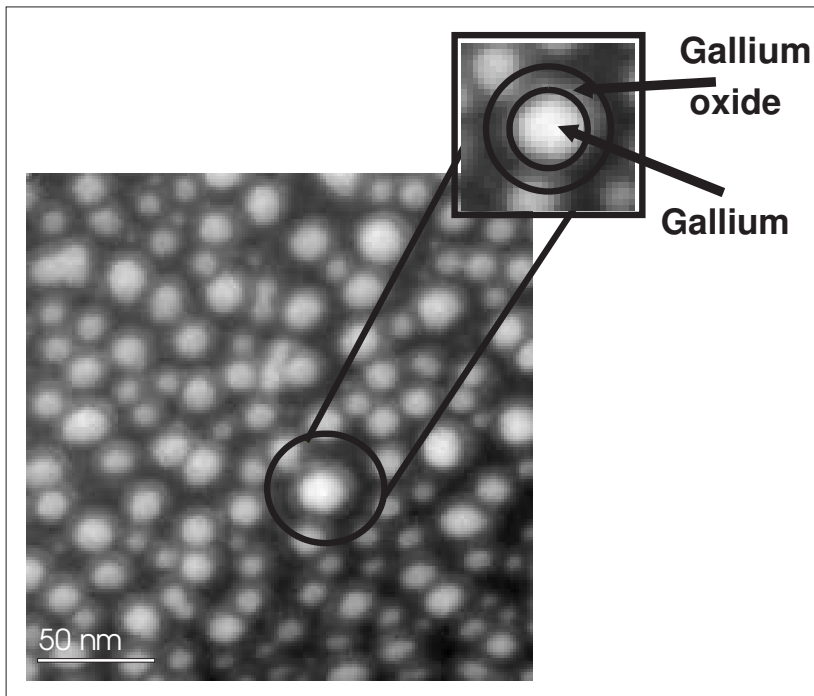


FIG. 5: SEnergy filtered TEM image of gallium nanoparticles on Si(100) formed after 100 min of deposition at room temperature. The energy filter (12 eV) was used to evidence the particle structure (core of gallium surrounded by oxide).